Multicomponent Silicate Glasses from Gels (Commemoration Issue Dedicated to Professor Sumio Sakka On the Occasion of His Retirement)

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REVIEW

Multicomponent Silicate Glasses from Gels

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The important technologies in the preparation of multicomponent silicate glasses by a sol-gel process using aqueous metal salt solutions as the source for modifier cations are discussed. The components introduced in a gel as aqueous metal salt solution remain in the liquid phase of a wet gel without being incorporated in the skeletal structure and partially extracted with the liquid by the syneresis during aging process. The rest of cations in the micropores of the gel migrates towards outer surface of the gel and precipitate when dehydration is proceeded. The reduction of this migration, which is essential to prepare a homogeneous glass, is made by promoting the precipitation of microcrystallites of the salt on the microporewalls of the gel by the replacement of an organic solvent such as acetone for the liquid in the micropores. This technique is effectively applied to the preparation of CdS quantum dots materials, gradient index glass rods with large geometry, etc.

KEY WORDS : Multicomponent Silicate Glasses/ Sol-Gel/ Gradient Index (GRIN) Glass Rod/ Quantum Dots/ Aging Process/ Skeltal Structure

1. INTRODUCTION

There are several multicomponent silicate glasses which are advantageously prepared by a sol-gel process over other techniques of glass preparation such as conventional melt-quenching technique, chemical vapour deposition, etc. Those include; (a) glasses containing a large amount of refractory materials such as Al_2O_3, TiO_2, ZrO_2, (b) glasses with a large amount of thermally unstable dopants such as non-oxide semiconductor materials, (c) gradient index glass rods of large geometry, etc.

The glasses of the first type are prepared by densifying gels obtained by the hydrolysis and polycondensation of metal alkoxides precursors.[1-7] The glasses of the second type are those having a relatively low softening temperature and prepared from gels obtained by hydrolyzing silicon alkoxide with aqeuous metal salt solutions as the sorce of modifyer oxides.[9-11] The glasses of the third type can be obtaine by either of the above techniques.[12-19]

The most important condition for preparing these glasses is that the gels obtained by the hydrolysis and polycondensation of the precursors are of high homogeneity. This is particularly true in the preparation of monolithic glasses. When we prepare binary or ternary silicate glasses from metal alkoxide precursor, we often encounter the heterogeneous precipitation of white powder due to the preferential hydrolysis of a particular aloxide.[20] The hinderence of such a precipitation is obviously one of the biggest issues to be overcome by elaborating the preparation

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of precursors. On the other hand, when we prepare multicomponent glasses from precursors containing metal salt solutions as the raw material of alkali or alkalin-earth oxides, we often encounter the crystallization of the metal salt on a gel surface upon drying.[21,22] The hinderence of such a crystallization is essential in the preparation of high performance optically functional glasses.

In the present paper, the key technology to prepare the monolithic multicomponent glasses from precursors consisting of silicon alkoxide and metal salt solution will be firstly discussed. Then, the application of the technique to the preparation of CdS quantum dots material and of gradient index glass rods will be introduced.

2. PARAMETERS AFFECTING THE GEL FORMATION

2.1. Solubility of a salt

In the preparation of a gel by the hydrolysis of tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) with aqeous metal salt solution, acetates are the most commonly used source of the salt because of their moderate solubility in water and their relatively low decomposition temperature upon heat treatment for the densification of the eventual gel. In this case, the solubility of the salt in alcohol is one of the parameters to be taken into consideration. If the solubility of the salt in alcohol is low, we often encounter the precipitation of the salt while hydrolyzing silicon due to the too drastic change of the solubility. This precipitation is avoided by using the aqeous solution of the concentration well below the saturation point. However, if the concentration is too low, the large shrinkage of a gel upon drying which often leads to the gel fracture is inevitable. Thus, the concentration of the starting materials and the kind of alcohol as the solvent of TEOS or TMOS are the factors to be considered.

Table 1. Solubility of acetates of representative modifier oxide in various solvents (mol/l).

Solvent \ Acetate	$Pb(OAc)_2$	NaOAc	KOAc	$Ca(OAc)_2$	$Ba(OAc)_2$
H_2O	1.3	5.6	26	2.4	2.0*)
MeOH	1.3*)	—	2.8*)	—	9.3×10^{-3} *)
EtOH	1.9×10^{-2} *)	2.6×10^{-1}	1.2*)	—	7.5×10^{-5} *)
iPrOH	3.9×10^{-3} *)	—	1.7×10^{-1} *)	—	1.5×10^{-7} *)
acetone	3.6×10^{-4} *)	—	2.5×10^{-7} *)	—	7.1×10^{-8} *)

*); Experimentally determined at Olympus Optical Co. Ltd.
Others are from LANGE'S HANDBOOK OF CHEMISTRY

Table 1 shows the solubility of acetates of representative modifyer oxide in various solvents. In general, the solubility decreases with increasing number of CH_2 units in the alcohol.

2.2. Gelation time

The hydrolysis and polycondensation of TEOS or TMOS is usually enhanced by existence of the salt and eventually the gelling time becomes shorter compared with the hydrolysis with distilled water.[21] This decrease in gelling time often leads to the bubble inclusion in the gel. Therefore, the control of gelling time to avoid the bubble inclusion is another issue to be concerned about.

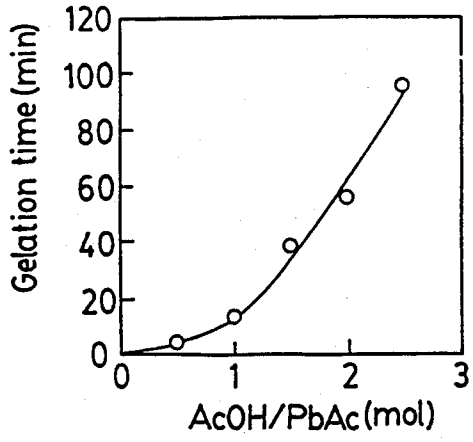

Fig. 1. Buffering effect of acetic acid on gelling time.

One of the ways to control the gelling time is to introduce an acid as the buffering agent. Figure 1 shows the effect of acetic acid on the control of gelling time of the system PbO-B_2O_3-SiO_2. The introduction of 2 mol of acetic acid per mol of lead acetate can retard the gelling time of the sol to twice of that without acid, thus enabling the hinderence of bubble inclusion in the eventual gel.

It should, however, be noted that the introduced acetic acid must be removed in the latter stage of the process to avoid the surface crystallization of lead acetate which tends to occure under the existence of excess acetate.[18]

3. EXTRACTION OF COMPONENTS BY THE SYNERESIS DURING AGING

3.1. Amount of separated liquid during aging

A gel formed in a proper containor begins to separate liquid by syneresis several tens of

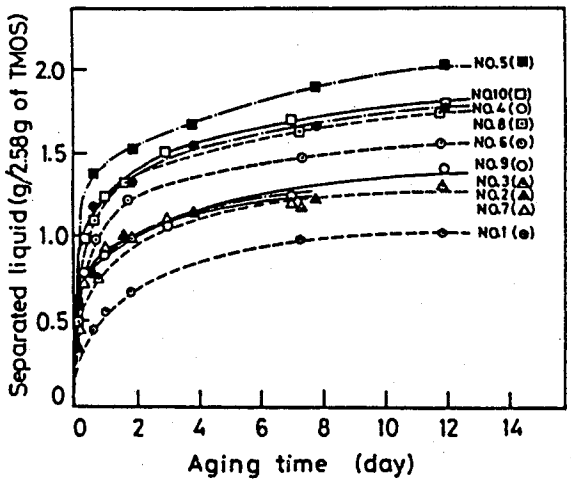

Fig. 2. Change in the amount of liquid separated by syneresis during aging of gels of xNa_2O-yB_2O_3-$zSiO_2$ system prepared from precursor solutions containing sodium acetate.

minutes after gelation. The separation of liquid rapidly occurs in the first 30 to 40 h and then slows down as shown in Fig. 2 on gels of Na_2O-B_2O_3-SiO_2 system of various compositions.[23] The samples NO. 1～3 and 7 contained smaller amount of sodium acetate, and therefore the smaller amount of water compared with the samples NO. 4～6, and 8～10. On the other hand, the amount of boron introduced as boron ethoxide, which yields ethanol by the hydrolysis, was relatively large on the samples NO. 1～5. In general, gels formed from precursor solutions with high water content separate a large amount of liquid.

3.2. Concentration of ions in the separated liquid

Fig. 3 and 4 show the dependence of concentration of sodium ions and boron in the separated liquid on aging time.[23] Although there is some scatter of the data points, the concentrations of both sodium ions and boron in the respective liquids are generally independent of aging time.

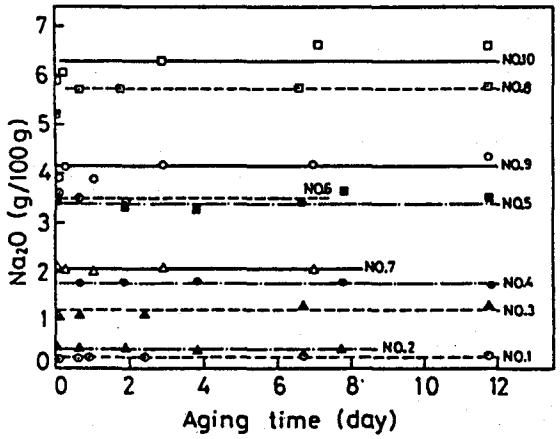

Fig. 3. Concentration of Na_2O in the liquid separated by syneresis from gels of xNa_2O-yB_2O_3-$zSiO_2$.

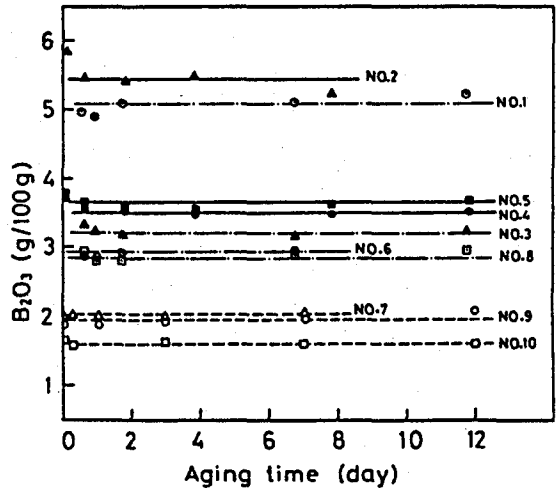

Fig. 4. Concentration of B_2O_3 in the liquid separated by syneresis from gels of xNa_2O-yB_2O_3-$zSiO_2$ system.

The concentration of sodium ion in the separated liquid is quite high on samples NO. 8～10 containing relatively large amount of water, whereas it is very low on samples NO. 1～4 containing relatively large amount of ethanol. This is due to the higher solubility of sodium acetate in water than in alcohol, i.e., 54.2 g/100 g of H_2O versus 16.0 g/100 g of MeOH and 4.51 g/100 g of EtOH at room temperature.

The concentration of boron in the separated liquid is high on the samples NO. 1～4 on the contrary, whereas it is relatively low on samples NO. 9 and 10 whose major constituent of liquid phase is not alcohol.

These results suggest that both sodium and boron are not incorporated in the skeletal structure of a gel but remain in the liquid phase or on the micropore walls as microcrystallites.

3.3. Loss of ions due to extraction by syneresis

Above results of the constant concentration of ions in the separated liquid suggests that the

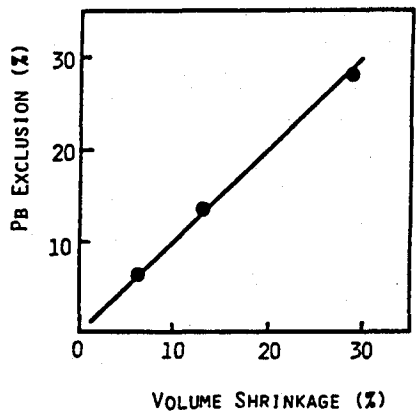

Fig. 5a. Relation between the amount of excluded lead ions and the volume shrinkage during syneresis of a gel.

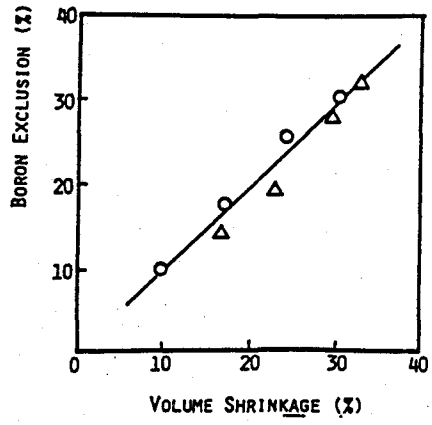

Fig. 5b. Relation between the amount of excluded boron and the volume shrinkage during syneresis of a gel. ○, H_3BO_3; △, $B(OC_2H_5)_3$.

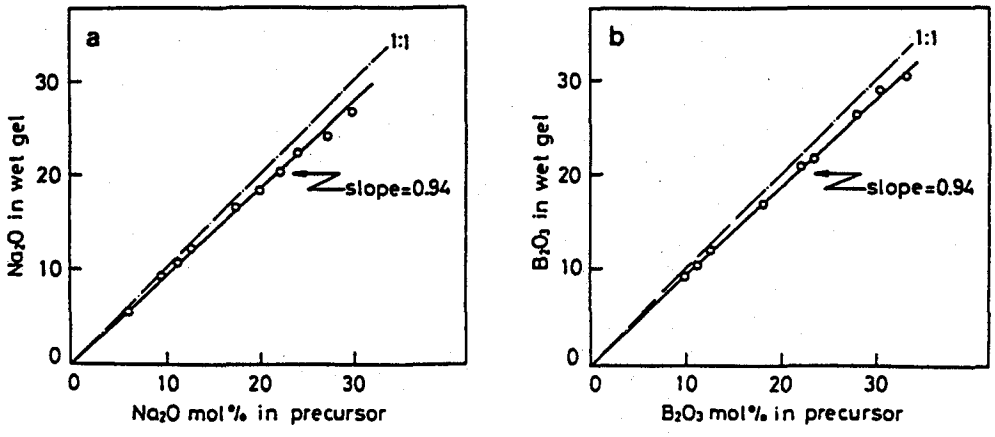

Fig. 6. Relation between sodium and boron concentrations in wet gels and those in precursor solutions: (a) sodium; (b) boron.

amount of ions lost in this stage is dependent of aging time, i.e., dependent on the volume shrinkage. This is depicted in Fig. 5(a) and (b) on the lead borosilicate system.[21] Thus, it is important to control the aging temperature and time to have a good reproducibility on the composition of a gel.

On the other hand, it was known by the preliminary study on sodium borosilicate system that at least 15 h of aging at room temperature was necessary in the preparation of monolithic gels in order to enhance the strength of a gel to avoid fracture during handling for subsequent treatments. Figs. 6(a) and (b) show the relation between the sodium and boron concentrations in the precursor solutions and those estimated for wet gels after the aging for 15 h based on the data in Figs. 2~4.[23] The slopes of 0.94 in the figures show that about 6% of sodium and boron are lost by this stage.

4. REDUCTION OF CATION MIGRATION DURING DRYING

4.1. Reduction of cation migration by replacing the liquid in the micropores by aceton

Cations in the micropores of a wet gel easily migrate or are carried with water toward the gel surface and precipitate there when dehydration of the gel is advanced, resulting in the formation of xerogels with highly concentrated modifier cations at the surface.[21,22] One of the effective methods to reduce this migration of cations is to replace water in the micropores by an organic solvent and promote the precipitation of microcrystallites of the salts on micropore walls by utilizing the change in solubility.[21,22] From the solubility data of various salts, acetone is one of the most popular organic solvent among those suitable to such treatment. Fig. 7 demonstrates the uniform concentration of lead in radial direction of a glass rod obtained by replacing acetone for water in a gel.[21]

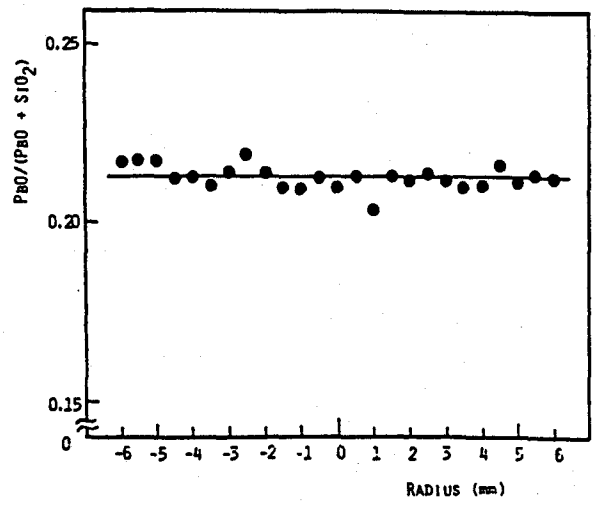

Fig. 7. Concentration of lead in the radial direction of the gel-derived Glass.

4.2. Loss of cations by the extraction of water and alcohol

One of the issues to be noted on this treatment is that some of the cations are carried with water and alcohol out of the gel. Therefore, the concentration of modifier ions further decrease

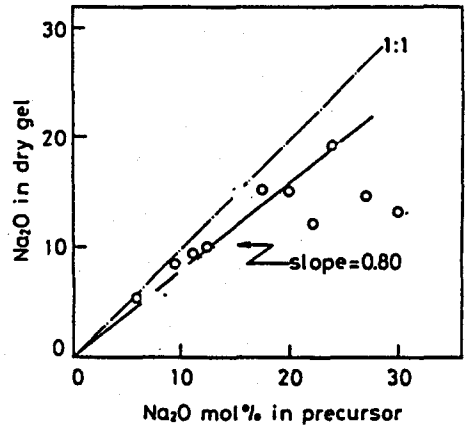

Fig. 8. Relation between sodium content in precursor solution and dry gels.

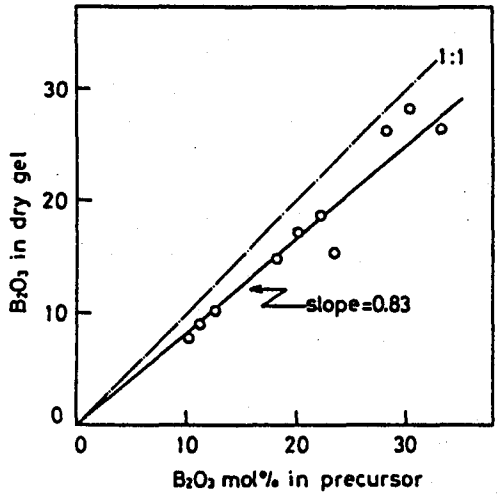

Fig. 9. Relation between boron content in precursor solution and dry gels.

from that in a wet gel. Fig. 8 and Fig. 9 respectively depict the relations between sodium and boron concentrations in precursor solutions and those in dry gels obtained by the replacement of acetone for liquid in the wet gels after aging for 15 h.[23]

The sodium contents in most of the dry gels are about 80% of those in precursor solutions, suggesting that about 14% of sodium was further lost by this treatment due to extraction with water and alcohol. It is known from the plots in Fig. 9 that about 11% of boron is further lost by the similar reason, resulting in the total loss of 17%.

There are some data points in Fig. 8 which largely deviated from the line with the slope of 0.80. These points are attributed to the crystallization of sodium acetate at the outer surface of the gel which occured due to too drastic change in solubility. The formation of surface crystal which peals off the gel during subsequent treatment or leads to the gel fracture tend to occure in the system with high sodium concentration above 20 mol%.

5. DESIGNING THE PRECURSOR SOLUTION FOR DESIRED GLASS

The results of chemical analysis for the gel-derived glasses were substantially similar to those for dry gels. The relationship between the compositions of final glasses and those of precursor solutions is, therefore, depicted by combining the data in Figs. 8 and 9 as shown in Fig. 10 in the case where the aging of gels is carried out for 15 h.[23] The composition of the glass will shift toward higher silica content side than these value if the aging time is longer because lager amount of liquid will separate.

Using these relations the designing of the precursor solution for a glass of soda-borosilicate system with a desired composition is easily made. For example , the composition of precursor solution for the glass of $15Na_2O{\cdot}15B_2O_3{\cdot}70SiO_2$(mol%) is designed to be $(15/0.8)Na_2O{\cdot}(15/0.83)B_2O_3{\cdot}70SiO_2$ or (30/0.8)NaAc·(30/0.83)$B(OEt)_3$·70TMOS (in mol).

The results for the test of this relationship, which are shown in Table 2 are satisfying within the fluctuation which are observed in conventional melt-quenching techniques.[23]

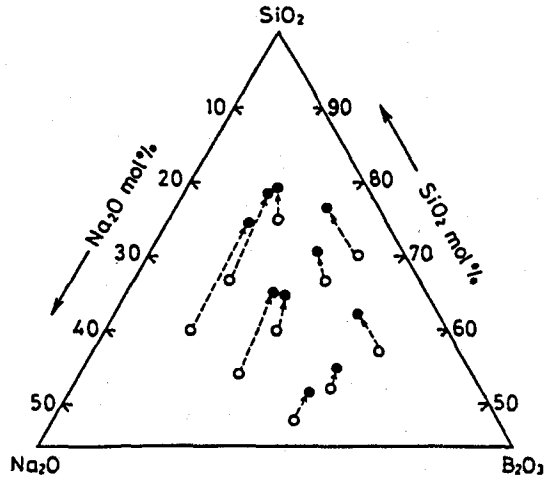

Fig. 10. Change in composition in the process to obtain monolithic dry gel: ○, precursor; ●, dry gel.

Table 2. Glass composition obtained from precursor solution designed according to the relationship.

Sample		Na_2O	B_2O_3	SiO_2
A	target	16	14	70[a]
	precursor	20 ±0.1	17.5±0.1	70 ±0.1
	result	14 ±0.3	13.6±0.1	72.4±0.2
B	target	15	18	67
	precursor	19 ±0.1	22 ±0.2	67 ±0.1
	result	14.5±0.3	18.5±0.2	67 ±0.1
C	target	15	25	60
	precursor	18 ±0.1	28 ±0.3	60 ±0.1
	result	15 ±0.3	25 ±0.3	60 ±0.1
D	target	20	25	55
	precursor	25 ±0.1	28 ±0.3	55 ±0.1
	result	17 ±0.4	25 ±0.3	58 ±0.1

[a] All numbers represent mol ratio.

6. APPLICATION

6.1. CdS quantum dots materials

Silicate glasses containing nanometer size semiconducter materials such as CdS, CdSe have recently received attention as they exhibit high non-linear susceptibility with fast response time. The glasses containing a large number of these thermally unstable semiconductor particles, which is essential for the high nonlinear susceptibility, are advantageously prepared by sol-gel process over the melt-quenching technique because of low temperature process. This is particularly true for alkali containing multicomponent system in which a gel can be densified at a temperature well below the decomposition point of the semiconductor materials.

One of the examples is the preparation of sodium borosilicate glasses containing CdS microcrystallites of the average size of 3~6 nm up to 8 wt%.[9,10] Gels were prepared from

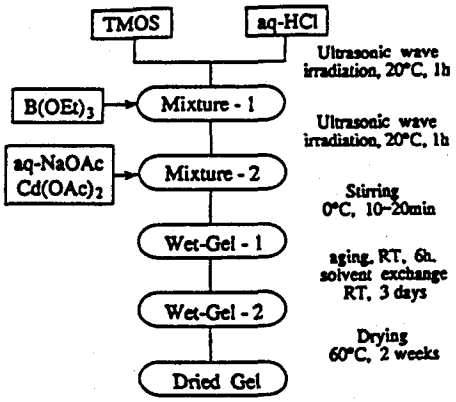

Fig. 11a. Flow chart of the preparation of CdO doped gel.

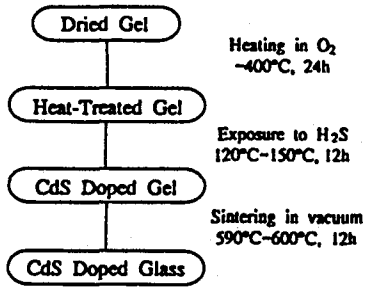

Fig. 11b. Optices flow chart for processing of CdO-containing gel to obtain CdS-doped quantum dots.

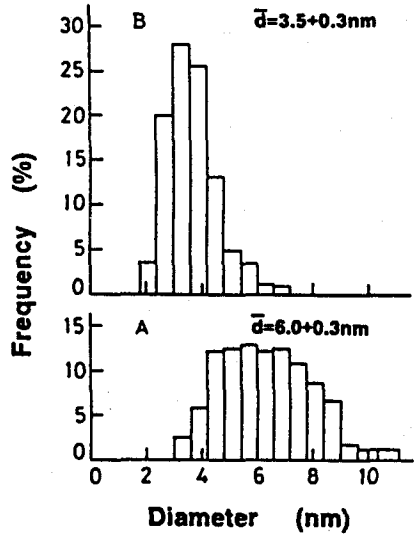

Fig. 12. Size distribution of CdS crystallites in glasses. CdS content: A, 8.0 wt%; B, 3.8 wt%.

precursor solution consisted of TMOS, boron triethoxide, aqueous sodium acetate solution and aqueous cadmium acetate solution. Then they were subjected to the treatment with acetone to precipitate microcrystallites of cadmium acetate as well as those of sodium acetate onto micropore walls of the gel. After being dried, the gels were subjected to pretreatment with oxygen at an elevated temperature, in order to convert the cadmium acetate into cadmium oxide. The gels were then exposed to hydrogen sulfide in order to convert cadmium oxide into cadmium sulfide, followed by sintering into pore free dense glasses at a temperature near 600°C. Fig. 11 shows the flow chart of this process.

The size distribution of CdS crystallites in the glasses obtained by this method is shown in Fig. 12. The third order non-linear susceptibility of these glasses in near resonance region were determined to be $1\sim6\times10^{-7}$ esu by degenerate four-wave mixing. These values are comparable with the highest value reported on melt-quenched glass. Further improvement of the nonlinear susceptibility is possible by optimizing the processing conditions. Moreover, it was recently disclosed by the pump and probe method that the gel-derived quantum dots glass is much more stable to the laser irradiation than melt-quenched glasses.[24]

6.2. Gradient index glass rods with large geometry

A radial gradient index (r-GRIN) glass rods in which refractive index changes in the radial direction in the manner given by Eq. (1) has peculior light propagation characteristics and provides many advantages over homogeneous lens.[19]

$$n(r)=n_0+n_1r^2+n_2r^4+n_3r^6+\cdots\cdots \quad (1)$$

where n_0 is the refractive index at the center axis of the rod, r is the radial distance from the axis, and n_1, n_2, n_3, are constants.

The preparation of r-GRIN lens of large size with large difference in the refractive index between the center and perifery can be advantageously made by sol-gel process over ion-exchange technique, the common method of r-GRIN manufacture. The preparation of a material of the diameter larger than several mm by ion-exchange is virtually impossible due to the low diffusion coefficients of index modifying cations in a solid glass. In addition, r-GRIN rods with low chromatic aberration are obtainable by a sol-gel process where the control of the concentration profiles of both single- and multi-valent cations is possible, whereas it is virtually impossible by the ion-exchange technique.

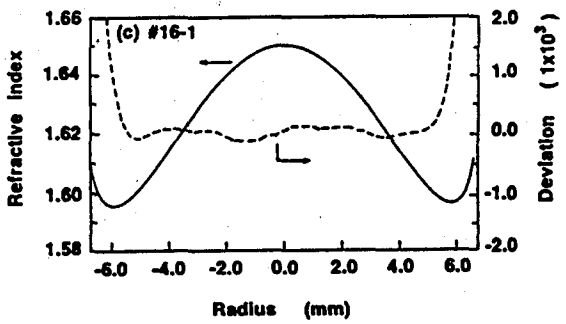

Fig. 13. Profiles of refractive index (solid line) and the deviation from regression curve (broken line) representing eq. (1)

Fig. 13 shows the refractive index profile in the *r*-GRIN rod of about 13 mm diameter prepared by the sol-gel process from the precursor solution containing TMOS, TEOS, boron triethoxide, aqueous lead acetate solution, aqueous HCl solution and acetic acid.[19] A wet gel of about 35 mm in diameter and 50 mm in length with the composition corresponding to the glass of $26PbO{\cdot}7B_2O_3{\cdot}67SiO_2$ (mol%) formed in a polypropylene vial was subjected to the treatments according to the flow chart shown in Fig. 14.[19]

The extraction of acetic acid in STEP-1 is to reduce acetate concentration in the liquid phase to avoid the surface crystallization in the subsequent replacement of solvent in STEP-2. The formation of concentration profile of lead to give the refractive index profile was made by immersing the gel having microcrystallites of lead acetate on the micropore walls into an ethanolic solution of potassium acetate, followed by fixing the profile by immersing the gel into acetone. The sintering temperature of the gel into a glass was about 500°C.

The refractive index profile in the GRIN rods thus obtained is nearly parabolic upto about

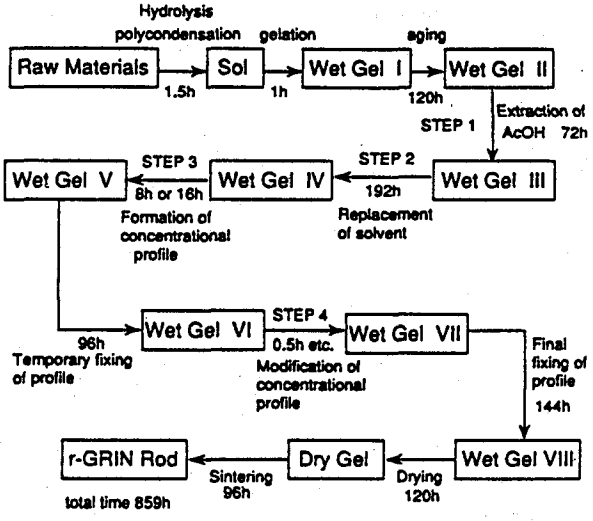

Fig. 14. Flow of the preparation of *r*-GRIN rods by the sol-gel process using lead acetate as the source of index-modifying cation.

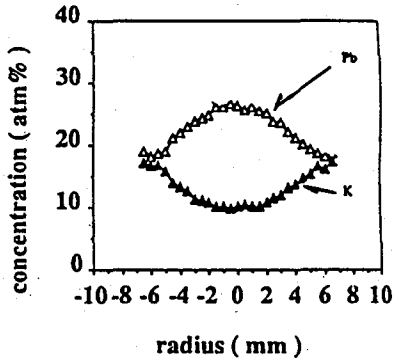

Fig. 15. Concentrational profiles of lead and potassium ions in the *r*-GRIN rods.

5 mm from the center axis but deviate thereafter, as shown in Fig. 13. This deviation is due to migration of lead ions during exchange of solvent for the fixing of the concentration profile. Although the process must be modified to minimize this deviation, the concentration profiles of lead and potassium in the eventual GRIN rods, which are shown in Fig. 15, show the potential of this method to the preparation of *r*-GRIN rod with large geometry and low chromatic aberration.

7. SUMMARY

The sol-gel process using aqeous metal salt solution is applicable to the preparation of optically and opto-electronically important multicomponent silicate glasses. The important technologies to obtain such glasses include the precise control of aging temperature and time, and reduction of the migration of ions during drying process.

ACKNOWLEDGEMENT

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REFERENCES

(1) B.E. Yoldas, *J. Non-Cryst. Solids,* **52**, 105 (1982).
(2) U. Wellbrock, W. Beier and G.H. Frischat, *J. Non-Cryst. Solids,* **147/148**, 350 (1992).
(3) M. Iwasaki, A. Yasumori, H. Kawazoe and M. Yamane, *J. Non-Cryst. Solids,* **121**, 147 (1990).
(4) M. Nogami and Y. Moriya, *J. Non-Cryst. Solids,* **48**, 359 (1982).
(5) C.J. Brinker and G.W. Scherer, *J. Am. Ceram. Soc.,* **69**, C12 (1986).
(6) S. Satoh, K. Susa and I. Matsuyama, *J. Non-Cryst. Solids,* **146**, 121 (1992).
(7) B.E. Yaldas, *J. Non-Cryst. Solids,* **38/39**, 81 (1980).
(8) S. Sakka and K. Kamiya, *J. Non-Cryst. Solids,* **42**, 403 (1980).
(9) T. Takada, T. Yano, A. Yasumori and J.D. Mackenzie, *J. Non-Cryst. Solids,* **147** & **148**, 631 (1992).
(10) M. Yamane, T. Takada, J.D. Mackenzie and Chia-Yen Li, *SPIE,* **1758**, 577 (1992).
(11) T. Takada, T. Yano, A. Yasumori and M. Yamane, *J. Ceram. Soc. Jpn.,* **101**, 73 (1993).
(12) K. Shingyouchi, S. Konishi, K. Susa and I. Matsuyama, *Electron. Lett.,* **22**, 99(1986).
(13) K. Shingyouchi, S. Konishi, K. Susa and I. Matsuyama, *Electron. Lett.,* **22**, 1108 (1986).
(14) S. Konishi, K. Shingyouchi and A. Makishima, *J. Non-Cryst. Solids,* **100**, 511 (1988).
(15) J.B. Caldwell, T.M. Che, R.W. Cruse, R.M. Mininni, R.E. Nikles, V.N. Warden and M.A. Banash, *Mater. Res. Soc. Symp. Proc.,* **180**, 727 (1990).
(16) M. Yamane, J.B. Caldwell and D.T. Moore, *J. Non-Cryst. Solids,* **85**, 244 (1986).
(17) M. Yamane, H. Kawazoe, A. Yasumori and T. Takahashi, *J. Non-Cryst. Solids,* **100**, 506 (1988).
(18) M. Yamane, A. Yasumori, M. Iwasaki and K. Hayashi, *Mat. Res. Symp. Proc.,* **180**, 717 (1990).
(19) M. Yamane and M. Inami, *J. Non-Cryst. Solids,* **147** & **148**, 606 (1992).
(20) M. Yamane, S. Inoue and K. Nakazawa, *J. Non-Cryst. Solids,* **48**, 153 (1982).
(21) H. Maeda, M. Iwasaki, A. Yasumori and M. Yamane, *J. Non-Cryst. Solids,* **121**, 61 (1990).
(22) M. Yamane, H. Kawazoe, A. Yasumori and T. Takahashi, *J. Non-Cryst. Solids,* **99**, 160 (1988).
(23) J. Chang, A. Yasumori and M. Yamane, *J. Non-Cryst. Solids,* **134**, 32 (1991).
(24) J.D. Mackenzie, *J. Ceram. Soc. Jpn.,* **101**, 1 (1993).